11-28-00   4

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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1 53(b))

Attorney Docket No.	KSU-189
First Inventor	Oleg Yaroshchuk
Title	Optical Compensation Film for Liquid Crystal Display
Express Mail Label No.	EL617150589US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

1. [X] Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)

2. [X] Applicant claims small entity status.
See 377 CFR 1.27.

3. [X] Specification   [Total Pages 29]
(preferred arrangement set forth below)
-Descriptive title of the Invention
-Cross Reference to Related Applications
-Statement Regarding Fed sponsored R & D
-Reference to sequence listing, a table,
or a computer program listing appendix
-Background of the Invention
-Brief Summary of the Invention
-Brief Description of the Drawings (if filed)
-Detailed Description
-Claim(s)
-Abstract of the Disclosure

4. [X] Drawing(s) (35 U.S.C. 113)   [Total Sheets 10]

5. [ ] Oath or Declaration   [Total Sheets 3]
   a. [X] Unexecuted (original or copy)
   b. [ ] Copy from a prior application (37 CFR 1.63 (d))
   (for continuation/divisional with Box 17 completed
      i. [ ] DELETION OF INVENTOR(S)
      signed statement attached deleting inventor(s)
      named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).

6. [X] Application Data Sheet. See 37 CFR 1.76

7. [ ] CD-ROM or CD-R in duplicate, large table or Computer Program (Appendix)

8. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
   a. [ ] Computer Readable Form (CRF)
   b. Specification Sequence Listing on:
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   c. [ ] Statements verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

9. [ ] Assignment Papers (cover sheet & document(s))

10. [ ] 37 CFR 3.73(b) statement
(when there is an assignee)   [ ] Power of Attorney

11. [ ] English Translation Document (if applicable)

12. [ ] Information Disclosure Statement (IDS)/PTO-1449   [ ] Copies of IDS Citations

13. [ ] Preliminary Amendment

14. [X] Return Receipt Postcard (MPEP 503)
(should be specifically itemized)

15. [ ] Certified Copy of Priority Document(s)
(if foreign priority is claimed)

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17. If a CONTINUING APPLICATION, *check appropriate box, and supply the requisite information below and in a preliminary amendment, or in an Application Data Sheet under 37 CFR 1.76:*
☐ Continuation   ☐ Divisional   ☐ Continuation-in-part (CIP)   of prior application No:_____
Prior application information: Examiner_____   Group/Art Unit:_____

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

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Signature	*(signature)*	Date	11-27-00

JC961 U.S. PTO   11/27/00

JC564 U.S. PTO   09/722991   11/27/00

PTO/SB/17 (08-00)
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FEE TRANSMITTAL
for FY 2000

Patent fees are subject to annual revision.

Complete if Known	
Application Number	
Filing Date	11/27/2000
First Named Inventor	Yaroshchuk, et al.
Examiner Name	
Group/Art Unit	

TOTAL AMOUNT OF PAYMENT	($) 355.00	Attorney Docket No.	KSU-189

METHOD OF PAYMENT (check one)

1. [X] The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee ($)	Fee Code	Fee ($)		
101	710	201	355	Utility filing fee	355.00
106	320	206	160	Design filing fee	
107	490	207	245	Plant filing fee	
108	710	208	355	Reissue filing fee	
114	150	214	75	Provisional filing fee	

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Independent Claims	3	- 3**=	0	X	40	= 0
Multiple Dependent				=		

**or number previously paid, if greater; For Reissues, see below

Large Entity		Small Entity		Fee Description
Fee Code	Fee ($)	Fee Code	Fee ($)	
103	18	203	9	Claims in excess of 20
102	80	202	40	Independent claims in excess of 3
104	270	204	135	Multiple dependent claim, if not paid
109	80	209	40	**Reissue independent claims over original patent
110	18	210	9	**Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($)0

FEE CALCULATION (continued)

3. ADDITIONAL FEES

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105	130	205	65	Surcharge – late filing fee or oath	
127	50	227	25	Surcharge – late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	390	216	195	Extension for reply within second month	
117	890	217	445	Extension for reply within third month	
118	1,390	218	695	Extension for reply within fourth month	
128	1,890	228	945	Extension for reply within fifth month	
119	310	219	155	Notice of Appeal	
120	310	220	155	Filing a brief in support of an appeal	
121	270	221	135	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive – unavoidable	
141	1,240	241	620	Petition to revive – unintentional	
142	1,240	242	620	Utility issue fee (or reissue)	
143	440	243	220	Design issue fee	
144	600	244	300	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	240	126	240	Submission of information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	710	246	355	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	710	249	355	For each additional invention to be examined (37 CFR § 1.129(b))	

Other fee (specify) _____

Other fee (specify) _____

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TRANSMITTAL SHEET FOR PATENT APPLICATION

Dear Sirs:

Transmitted herewith for filing under 35 U.S.C. §111(a) is a written application for a patent.

Express Mail No.: EL617150589US

Title: Optical Compensation Film for Liquid Crystal Display

Inventors: Oleg Yaroshchuk, Yuri Reznikov, Jack Kelly, Liang-Chy Chien, Tatiana Sergan

Docket No.: KSU-189

Enclosed is:

Transmittal Letter with Certificate of Mailing and Authorization to Charge Deposit Account (2 pages - in duplicate)
Utility Patent Application Transmittal Sheet (1 page)
Fee Transmittal Sheet (1 page - in duplicate)
Print EFS Bibliographic Data Sheet
Combined Declaration and Power of Attorney (3 pages - unexecuted)
Specification:

25	pages of Description
3	pages of Claims
1	page of Abstract
10	pages of Drawings
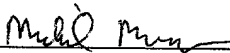
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Respectfully submitted,

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Date

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STATEMENT CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) & 1.27(d))—NONPROFIT ORGANIZATION	Docket Number (Optional) KSU-189

Applicant, ~~Patentee, or Examiner~~: Jack Kelly, et al.

Application ~~or Patent~~ No.: _____

Filed ~~or Issued~~: _____

Title: Optical Compensation for Liquid Crystal Display

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TITLE IN ORGANIZATION OF PERSON SIGNING   Vice Provost and Dean of Research & Graduate Studies

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APPLICATION INFORMATION

Title Line One:: Optical Compensation Film for Liquid Cry
Title Line Two:: stal Display
Total Drawing Sheets:: 10
Formal Drawings?:: Yes
Application Type:: Utility
Docket Number:: KSU-189
Secrecy Order in Parent Appl.?:: No

REPRESENTATIVE INFORMATION

Registration Number One:: 26519
Registration Number Two:: 28837
Registration Number Three:: 36010
Registration Number Four:: 22325
Registration Number Five:: 22353
Registration Number Six:: 24926
Registration Number Seven:: 27182
Registration Number Eight:: 29096
Registration Number Nine:: 37400
Registration Number Ten:: 40139
Registration Number Eleven:: 42859
Registration Number Twelve:: 42906
Registration Number Thirteen:: 43921
Registration Number Fourteen:: 46069

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OPTICAL COMPENSATION FILM FOR LIQUID CRYSTAL DISPLAY

FIELD OF THE INVENTION

5   The present invention is directed to optical compensation films for liquid crystal displays. More particularly, the invention is directed to optical compensation films formed from polymers that have been irradiated by light.

BACKGROUND OF THE INVENTION

10

Compensation films are an indispensable component of modern liquid crystal displays (LCDs). Compensation films, for example, can compensate the color background of super-twisted nematic LCDs, and can expand the viewing angle of twisted nematic LCDs. The main idea of the optical compensation film (OCF) 15 design is to make the optical symmetry of the compensator more closely resemble that of the director distribution in the liquid crystal layer in the selected state. Therefore, certain parameters of the OCF are determined by the type of LCD mode.

Both negative and positive compensation films, with optics axes oriented in-plane, tilted and normal to the plane of the film, have been developed. In order to 20 adjust more precisely to the director distribution in the liquid crystal (LC) cell, in the modern OCF, the optical axis that is modulated over the film thickness or structure of the OCF is biaxial. Alternatively, a stack of uniaxial films with different directions of optical axis could be used.

25

Conventional optical compensation films are produced from polymer materials. The OCFs in general use are stretched polycarbonate, yielding negative retardation, and polystyrene, yielding positive retardation, films. These compensators have almost the same wavelength dispersion as that of the liquid 30 crystals and the compensators have high optical anisotropy. The main drawback of stretched films is that it is rather difficult to produce the uniform retardation over a large area and to control the optical axis direction.

Another approach is the use of polymer liquid crystalline films. Cholesteric polymer films are used for the color compensation of LCDs. Discotic compound films expand viewing angle of LCDs. Discotic films possess high negative

5   birefringence and have similar orientation structure to that of the on-state LCD. Uniform alignment of LC layers is usually induced with aligning substrates or external field. The obtained structure is usually fixed by photo-crosslinking or polymerization process. The main problems of the application of liquid crystalline films are the complication of their alignment and high commercial cost.

10

What is needed in the art is a method of fabricating an optical compensation film wherein the alignment in the film is reached without stretching, application of electric and/or magnetic fields, or special treatment of the aligning substrates, and which can form a uniform retardation over a large area.

15

It is therefore an object of the invention to provide a method of fabricating an optical compensation film for a liquid crystal display without stretching, application of an electric and/or magnetic field, or special treatment of the aligning substrates.

20

SUMMARY OF THE INVENTION

The present invention provides an optical compensation film for a liquid crystal display comprising a polymer capable of producing light induced anisotropy

25   characterized in that the polymer has been irradiated with light to form at least one optical axis.

The present invention also provides a method of making an optical compensation film comprising: providing a substrate; disposing a polymer in a

30   solvent on the substrate; removing the solvent to form a polymer film; and irradiating the polymer with light, wherein at least one optical axis is formed in the polymer film.

2

The present invention also provides a method of making a liquid crystal display cell containing an optical compensation film comprising: providing two opposed substrates, disposing the optical compensation film on at least one of the substrates on a surface of the substrate that faces the other substrate, irradiating the optical compensation film with light, disposing electrodes at one of i) on the substrate prior to disposing the optical compensation film, and ii) on the optical compensation film, disposing a liquid crystal between the substrates, and sealing the substrates together, wherein at least one optical axis is formed in the polymer film.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows structural formula of the polymers used in our examples

Figure 2 is a scheme of the ellipsometry set up.

Figures 3A and 3B are $\varphi(\theta)$ graphs for the azopolymer 1 (Fig.1a) film before (Fig. 3A) and after (Fig. 3B) irradiation with polarized UV light.

Figure 4 is a graph of birefringence kinetics in azopolymer 1 (Fig.1b) under polarized UV light irradiation.

Figures 5A and 5B are $\varphi(\theta)$ graphs for the azopolymer 2 (Fig.1b) film before (Fig. 5A) and after (Fig. 5B) irradiation with polarized UV light.

Figure 6 is a graph of birefringence kinetics in azopolymer 2 under polarized UV light irradiation.

Figure 7 presents φ versus θ curves measured for the film of azopolymer 2 obliquely irradiated with non-polarized UV light. The angle of light incidence is 45°.

Figure 8 presents $\varphi(\theta)$ graphs for polyvinylcinnamate film irradiated with polarized UV light.

Figure 9 shows irradiation schemes and induced orientational structures for

5   A) positive A plate ($n_y > n_x = n_z$), B) negative A plate ($n_x < n_y = n_z$), C) biaxial film ($n_x \neq n_y \neq n_z$), D) positive C plate ($n_z > n_x = n_y$), E) positive O plate.

Figure 10 is a schematic of a liquid crystal cell.

10   DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an optical compensation film for a liquid crystal display. The optical compensation film is an organic material capable of producing light induced anisotropy. The film is irradiated with light to form an 15   optical axis.

Classes of materials that can function as the optical compensation film in the present invention include, but are not limited to, photosensitive polymers, such as polyimides; methacrylates; acrylates; vinyls; vinyl ethers; siloxanes; styrene; epoxy 20   polymers containing azobenzene, stilbene, cinnamate, maleimide, or coumarin functional groups in the side and/or main polymer chain; and mixtures thereof.

Specific polymers that can function as the optical compensation film in the present invention include, but are not limited to, comb polymers containing 25   azobenzene or cinnamate derivatives in the side chain.

The average molecular weight of the polymers of the present invention range from about 10,000 to about 300,000. The preferred molecular weight is dependent upon the specific polymer selected. As used throughout this specification, the 30   molecular weight is weight average molecular weight.

4

The optical compensation film can then be incorporated into a liquid crystal cell. A liquid crystal cell typically comprises opposed substrates, electrodes on the substrates, an optical compensation film disposed over at least one of the electrodes, spacers between the substrates to control the thickness of the liquid crystal cell, and

5   liquid crystals disposed between the substrates. Figure 10 is a schematic of a typical liquid crystal cell. Layers 11 and 15 represent the combined substrate and electrodes. Layers 12 and 14 represent the optical compensation films. Layer 13 represents the liquid crystal material. And, layer 16 is a voltage source to power the cell.

10

The substrate can be any material commonly used for fabricating liquid crystal cells. Materials such as glass, quartz or plastic can be used. The substrate materials can also be any materials commonly used for fabricating chips, for example silicon

15

The electrodes of the liquid crystal cell can be fabricated from any material known to be used for electrodes for liquid crystal cells. Suitable materials for the electrodes include, but are not limited to, indium-tin-oxide (ITO), stannic oxide SnO_2, aluminum, chromium, silver, or gold.

20

SPECIFIC EMBODIMENTS OF THE INVENTION

As material for retardation films we used azopolymers and cinnamates. Structural formulae of the used polymers are shown in Fig.1. Both materials were

25   comb-like polymers with azobenzene fragments in the side chains connected by flexible alkyl spacers to the polymer backbone. Side chains of the azopolymer 1 (Fig. 1A) contained polar NO_2 groups. The side chains in azopolymer 2 (Fig. 1B) have hydrophobic alkyl groups C_6H_{13} attached to the azobenzene moiety. The difference in the chemical structure of the side chains was expected to influence the

30   difference in the supramolecular structure of azobenzene moieties. Due to flexibility of alkyl spacers, the azobenzene fragments could rotate relatively freely

in the polymer matrix. Since their concentration in the polymer was high enough, they could form mesophases within some temperature intervals.

Azobenzene fragments of azpolymer 1 (Fig.1A) formed smectic A and nematic mesophases within the temperature range 44°-52°C and 52°-55°C, respectively. The azopolymer 2 (Fig.1B) demonstrated a reentrant nematic mesophase within the temperature interval 112°-140°C. Both cinnamates were amorphous polymers. All polymers were solids at room temperature. The molecular weight of azopolymer 1 was about 13,500, and the molecular weight of azopolymer 2 was about 36,000.

The azopolymer films were fabricated by a spin coating technique. Azopolymer 1 and azopolymer 2 were dissolved in toluene and dichloroethane, respectively, up to concentrations of 10% by weight. The solutions were spin coated on glass substrates at spinning speeds of 1500-3000 rpm. The thickness of the films was measured with a profilometer manufactured by Tencor Instruments.

To induce the anisotropy in the samples of azopolymers, we used the light of a Xe lamp from Oriel Corp. The density of polarized irradiation used in the experiments was 11 mW/cm^2 in the wavelength range of 326-400 nm. UV light was polarized using dichroic UV polarizer supplied by Oriel Corporation and operable in the wavelength range of 230-770 nm.

The main photochemical reaction in azopolymers was trans-cis isomerization, whereas in cinnamate polymers it was (2+2') photocycloaddition of cinnamoyl units. The photoinduced anisotropy in polymers results from the light induced orientational ordering of photosensitive fragments and products of photochemical reaction.

To measure the light induced birefringence in polymer films, we used a transmission ellipsometry technique with fixed positions of a polarizer, quarter wave compensation plate and rotated analyzer (Figure 2). The quarter wave plate

converts the elliptically polarized light passing through the sample into linearly polarized light. The rotation angle of the polarization plane of testing light after phase plate could be found by rotation of the analyzer to a position of minimum light transmission at an angle φ. Let us assume that principle dielectric axes of the

5   film, x, y, and z, are oriented as it is shown in Fig.9. In case of oblique light incidence, the angle φ depends on the in-plane retardation $(n_y-n_x)d$, the out-of-plane retardation $(n_z-n_x)d$ and the absolute value of one of the refractive indices of the biaxial film, for example, n_x (d and λ are film thickness and light wavelength, respectively). The angle φ was calculated as a function of light incidence angles θ

10   of the testing beam assuming a certain sample configuration. Such calculations were carried out using Berreman's 4x4 matrix method. The experimental curves $\varphi(\theta)$ were fitted with the theoretical one. The absolute value of the refractive index measured by Abbe refractometer was used in the fitting process.

15   The setup included a low power He-Ne laser (λ=632.8 nm), two calcite Glan-Thompson polarizers mounted on rotational stages from Oriel Corp., a Babinet-Soleil compensator adjusted to produce the same retardation as a quarter wave plate for the light wavelength of λ=632.8 nm and a sample holder mounted on the rotational stage by Oriel Co. The light intensity was measured with a

20   photodiode connected to a Keithley Instuments multimeter. The setup was automatically controlled by a personal computer. The rotation accuracy was better than 0.2°.

25   In Figure 2, a helium neon laser (11) generates a light source. The light source passes through polarizer (12), sample (13), quarter wave plate (14), analyzer on rotational stage (15), and lens (16), before reaching detector (17).

The examples below illustrate abilities of this technique for the investigation of spatial orientational structures in the polymers used.

30

<u>Films of azopolymer 1</u>. The φ versus θ curves for azopolymer 1 (Fig.1a) before and after irradiation are presented in Fig. 3 a and Fig.3 b, respectively. In case of the non-irradiated film there was no phase shift for normal light incidence $(\theta=0)$. This indicated equality of the two in-plane indices: $n_y=n_x$. The film possessed out of plane birefringence $(n_z-n_x)d=-40$ nm that caused a phase shift at oblique light incidence. Curve fitting gave the out-of-plane index n_z as smaller than the two in-plane indices: $n_z<n_x=n_y$ and $n_z-n_x\sim -0.08$. The film showed negative birefringence with the optic axis perpendicular to the film surface (negative C film). The relationship between the three indices suggests that the azobenzene fragments are randomly distributed in the plane of the film with no preferred direction for their orientation (a degenerate in-plane distribution).

Fig. 3b show the curves $\varphi(\theta)$ measured after 15 min of UV light irradiation with the intensity of 20 mW/cm^2. Curves 1 and 2 correspond to vertical and horizontal azimuths of actinic UV light polarization, respectively. According to the modeling, positive phase shift corresponds to the axis in the horizontal direction having the higher in-plane refractive index n_y perpendicular to UV light polarization and the lower in-plane index n_x. Curve fitting for this case gave the following relationship between the three refractive indices: $n_y-n_x=0.3$ $((n_y-n_x)d\approx30$ nm$)$, $(n_z-n_x)d=0$ nm, $n_y>n_x=n_z$. The light induced structure was positive uniaxial with the optic axis perpendicular to the UV light polarization. In this case, the azobenzene fragments showed planar alignment perpendicular to the UV light polarization.

We studied kinetics of orientation of azobenzene fragments under polarized UV light irradiation with a light intensity of 20 mW/cm^2. Birefringence measurements were taken at the same irradiation site after successive periods of irradiation. The time between the finish of each irradiation step and taking the birefringence measurement was long enough to reach equilibrium. Figure 4 shows the measured values of induced in-plane and out-of-plane optical retardation $(n_y-n_x)d$ and $(n_z-n_x)d$, respectively, versus time of irradiation. Before the UV light was applied, the azobenzene fragments were distributed uniformly in the plane of the

film ($n_z < n_x = n_y$). The irradiation of azopolymer 1 redistributed the fragments in the plane of the film such that they aligned perpendicular to the direction of UV light polarization. This process increased the difference between two in-plane refractive indices. At the photosteady state, the film was a positive uniaxial medium with the

5   in-plane optic axis perpendicular to the UV light polarization $n_y > n_x = n_z$. . The value of induced birefringence n_y-n_x was higher than *0.25*. At the intermediate stages of irradiation the biaxial structures were detected.

Films of azopolymer 2. The φ versus θ curves for azopolymer 2 (Fig.1b)

10   before and after 15 min irradiation are presented in Fig. 5A and Fig.5B, respectively. Similar to the azopolymer 1, the in-plane birefringence was negligibly small n_y-n_x *≈0*. At the same time, the film was characterized by positive out-of-plane birefringence: *(n_z-n_x)d=35 nm (n_z-n_x ~ 0.085)* and $n_z > n_x = n_y$. . So, the film of the azopolymer 2 was a positive uniaxial medium with the optic axis normal to the

15   film surface.

For film of azopolymer 2, similar to the film of azopolymer 1, the higher index n_y was perpendicular to the direction of UV light polarization. However, the relationship between the three principal indices is different: n_y-n_x≈0.025 ((n_y-n_x)d≈10

20   nm) and n_z-n_x ≈ 0.12 ((n_z-n_x)d=50 nm), $n_z > n_y > n_x$. Without being limited to theory, this suggests a biaxial structure characterized by the fan-like distribution of the azo-benzene fragments in the plane that is perpendicular to the direction of light polarization.

25   Dependencies of (n_y-n_x)d and (n_z-n_x)d versus time of irradiation are presented in Fig.6. Increase of irradiation dose led to non-monotonous change of the in-plane birefringence n_y-n_x. Simultaneously, the out-of-plane birefringence n_z-n_x increased to *0.3* ((n_z-n_x)d=70 nm). The photosteady state was characterized by the high ordered uniaxial homeotropic alignment of the azobenzene fragments.

30

The φ versus θ curves measured for the film of azopolymer 2 obliquely irradiated with UV light are presented in Figure 7. The light incidence angle is $45°$. The film was fitted within uniaxial model with the inclination of the optic axis of $19°$ from the film normal. The birefringence value n_e-n_o was about 0.25.

5

The studies of orientational kinetics in the two types of polymers under polarized UV light irradiation indicated the differences in orientational behavior of the azobenzene fragments depending on chemical structure of main and side chains. The azobenzene fragments with polar groups retained their preferred in-plane

10   alignment. Irradiation by polarized UV light induced planar alignment of the fragments in the direction perpendicular to the direction of light polarization. The azobenzene fragments with alkyl functional groups preferred the homeotropic alignment. Small in-plane birefringence induced by low dose polarized light was transient. The photosteady state for this polymer was characterized by highly

15   ordered homeotropic alignment. Note that photo-steady state for both polymers was uniaxial. This uniaxiality could be connected with mesomorphic properties of the azobenzene fragments.

The illumination of the films of azopolymer 2 with polarized light induced

20   fan-like structures with small in-plane birefringence and preferred out-of-plane alignment of the azobenzene fragments. The illumination of this polymer with high UV doses provided highly ordered homeotropic alignment featuring high out-of-plane birefringence. The irradiation of the films of azopolymer 1 with polarized light provided planar alignment of the azobenzene fragments in the direction

25   perpendicular to the UV light polarization featuring high in-plane birefringence. The process of the induction of anisotropy had saturation behavior. The photosteady structures observed in both polymers were uniaxial.

Without being limited by theory, the in-plane distribution of azobenzene

30   fragments in azopolymer 1 can be explained by assuming in-plane alignment of the backbones and an interaction of the polar NO_2 group of the azobenzene moiety with the main chain fragments. The preferred homeotropic alignment of the azobenzene

10

fragments of the azopolymer 2 may possibly be determined by the hydrophobic functional group at the end of the moiety and its weak interactions with the polymer backbones.

5   The irradiation of polymer films with polarized UV light at normal incidence induced in-plane birefringence and changed the relationship between the three principal refractive indices in both polymers.

Polyvinylcinnamate films. The $\varphi(\theta)$ graphs for PVCN (Fig.1 c) film
10   irradiated with polarized light are presented in Figure 8. These curves were fitted well at the parameter set $(n_y-n_x)=23$ nm, $(n_z-n_x)=23$ nm, $(n_x< n_y=n_z)$ which corresponded to the model of negative A film.

The examples presented bellow classify the anisotropic structures which can
15   be induced with the light in photosensitive polymers.

In one embodiment of the present invention, the optical axis of the optical compensation film OO' lies in the plane of the polymer film perpendicularly to the direction of the preferential light polarization. When the refractive index in the
20   direction OO' is higher than in any other direction, l≠OO' a positive A film is formed (Figure 9a). When fabricating this film, the light beam is perpendicular or slantwise with respect to the plane of the polymer film. The light can be linearly polarized, elliptically polarized, or partially polarized. The film thickness is much less than the characteristic absorption length, i.e., the light intensity is constant in
25   the film. The polymer material can possess any of the effects resulting in light-induced anisotropy. It can be reorientation of photosensitive fragments perpendicular to the polarization of actinic light and/or light-induced photo-transformation of photosensitive fragments of polymer (decomposition, cross-linking, irreversible trans-cis isomerization etc).

30

The phenomenon of light induced anisotropy refers to materials having ability to show birefringence and dichroism when they are illuminated by actinic

light.   The parameters of the induced anisotropy depend on the irradiation conditions; direction of the induced axis of anisotropy depends on the direction of polarization of exciting light, while the value of the induced birefringence and dichroism on the irradiation dose.

5

In these conditions the direction of the anisotropy axis is determined by the direction of preferable polarization of light.   In most cases the light-induced anisotropy axis is perpendicular to the polarization E (azobenzene, stilbene, cinnamate based polymers, polyimides).   Some polyimide- and cinnamate-based

10   materials provide anisotropy axis parallel to the polarization of light.   The sign of birefringence is determined by chemical structure of the photosensitive fragments and the value of birefringence is given by the exposure time and light intensity.

Example 1

15   Material: Structural formula of the material is given by
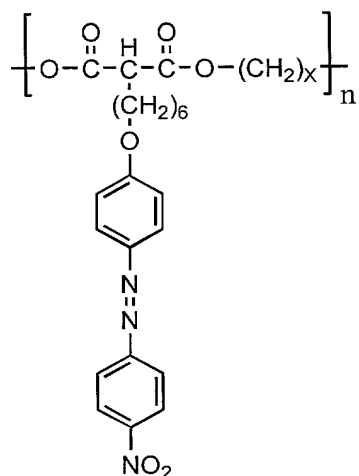
wherein x is a number from about 4 to about 16 and n is a number from about 10 to about 1000. In this example, x is 8 and the average molecular weight is 13500

20   g/mol. Synthesis of this material is described in *Makromol. Chem.*, 194, 3341 (1993) by A. Bohme, E. Novotna, H. Kresse, F. Kuschel and J. Lindau. This polymer absorbs light with λ less than about 500 nm due to an azobenzene

chromophore contained in the side-chains of polymer molecules. When absorbing light, the azobenzene fragments undergo trans-cis isomerization accompanied with reorientation perpendicularly to the light polarization. An optical dipole moment of the trans isomer is oriented almost along its long axis.

5

Fabrication of the polymer film:

The material above is dissolved in a dichloroethane (weight concentration of 40 g/1). A droplet of this solution is deposited on a rectangular glass substrate and spin-coated for 10 seconds at 2000 rpm. Then the substrate is maintained for 2 hours at 50°C to remove the solvent. As a result, a uniform polymer film with a thickness of about 0.4 μm is produced on the substrate.

Irradiation of the polymer film:

The film was irradiated with the parallel beam of the polarized light from a Xe-lamp. The light beam was perpendicular to the plane of the polymer. Light intensity in the plane of the substrate was 11 mW/cm^2. The film was exposed for 15 min. The irradiation spectrum of the lamp overlaps the absorption spectrum of the polymer film.

Characteristics of the film:

3D structures in the films were characterized by null ellipsometry technique. These measurements showed uniaxial structure with orientation of the optical axis in the plane of the film perpendicularly with respect to the direction of light polarization, Figure 9 (a). The estimated in-plane, photo-induced birefringence was n_y-$n_x = 0.3$.

Example 1a
Material: The same as in Example 1.
Fabrication of the polymer film: The same as in Example 1.

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Irradiation of the polymer film: The film was irradiated normally to the film plane with the parallel beam of the partially polarized or elliptically polarized light from a Xe-lamp. The other conditions are the same as in Example 1.

5 Example 1b

Material: The same as in the Example 1.

Fabrication of the polymer film: The same as in the Example 1.

Irradiation of the polymer film: The film was irradiated in tilt position with respect to the film plane with the parallel beam of the polarized, partially polarized or

10 elliptically polarized light from a Xe-lamp. The other conditions are the same as in Example 1.

In a second embodiment of the present invention, the uniaxial structure was induced when the optical axis OO' of the optical compensation film layed in the

15 plane of the polymer film along the direction of the preferential light polarization, and $n_{OO'} < n_{\perp OO'}$ (negative A film shown in Figure 9(b)). When fabricating this film, the light beam was perpendicular to the plane of the polymer film. The light can be linearly polarized, elliptically polarized, or partially polarized. The film thickness was much less than the characteristic absorption length, i.e., the light intensity was

20 constant in the film. The material possessed various effects, such as reorientation of photosensitive fragments perpendicular to the polarization of actinic light, and/or light-induced photo-transformation of photosensitive fragments of polymer (decomposition, cross-linking, irreversible trans-cis isomerization etc) resulting in light-induced anisotropy.

25

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Example 2

Material: Structural formula of the material is given by.

$$-\left(\!CH_2\!-\!\underset{\substack{|\\O\\|\\O=C\\|\\CH\\\|\|\\CH}}{CH}\!\right)_{\!\!n}-$$
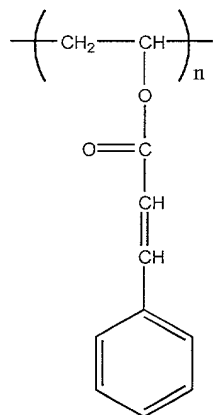
wherein n is a number from about 10 to about 1000. For this example, the average molecular weight was about 200,000. This polymer contains cynnamoyl groups in 5 the side chains, which are capable for both (2+2') photocycloaddition and trans-cis isomerization under irradiation with actinic light.

Fabrication of the polymer film:

The material was dissolved in dichloroethane at a weight concentration of 60g/l. A 10 droplet of this solution was deposited on a rectangular glass substrate and spin-coated for 10 seconds at 1500rpm. The substrate was maintained at 70°C for 2 hours to remove the solvent. A uniform polymer film with a thickness of about 1 µm was produced on the substrate.

15 Irradiation of the polymer film: The same as in Example 1.

Characteristic of the film:

The direction of the optical axis as well as the value of the induced birefringence in the film was determined by null ellipsometry technique. These measurements 20 showed uniaxial structure with orientation of the optical axis in plane of the film in the direction of light polarization. Refractive index in the direction of the optical axes is less then in any other direction (Fig.9b). Estimated in-plane photo-induced birefringence $n_y\text{-}n_x$ was as high as 0.01. This value is about an order of magnitude smaller than in Example 1.

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Example 2a

Material: The same as in Example 2.

Fabrication of the film: The same as in Example 2.

Irradiation of the film: The film was irradiated in the tilt position with respect to the film plane with the parallel beam of the polarized, partially polarized, or elliptically polarized light from a Xe-lamp. The other conditions were the same as in Example 2.

Example 2b

Material: Structural formula of the material is given by

$$\left(\!-CH_2\!-\!\underset{\displaystyle \substack{O \\ | \\ O\!=\!C \\ | \\ CH \\ \| \\ CH}}{CH}\!-\!\right)_n$$

(with a para-fluorophenyl ring attached to the CH)
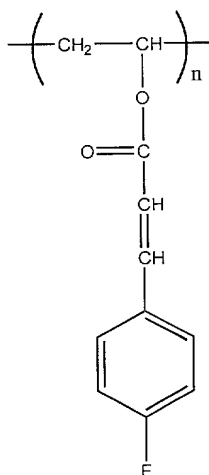
wherein n is a number from about 10 to about 1000. For this example, the molecular weight is 60,000.

Fabrication of the polymer film: The same as in Example 1.

Irradiation of the polymer film: The same as in Example 2.

16

Example 2c

Material: Mixture of two azopolymers with the structures shown below.
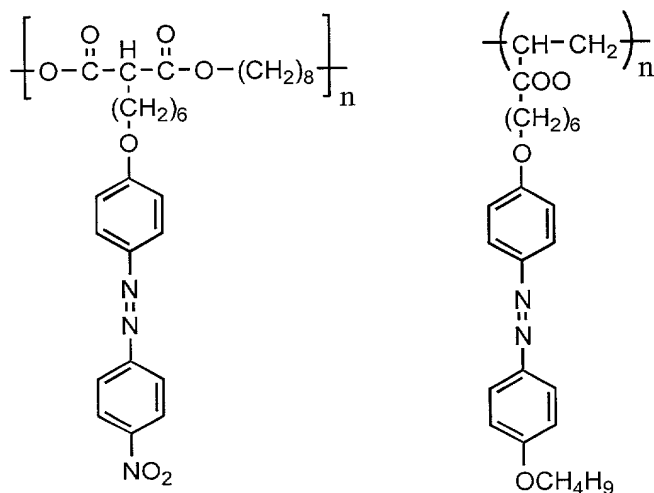
wherein each n is independently a number from about 10 to about 1000. For this

5   example, the structure at the left had a molecular weight of about 13,500 g/mol, and

the structure on the right had a molecular weight of about 36,000 g/mol. The

proportion of the materials in the composition was 4:1 by weight based on the

structure to the left to the structure at the right.

Fabrication of the film: The same as in Example 1.

10   Irradiation of the film: The same as in Example 1.

Characteristics of the film: The photoinduced structure was a uniaxial negative A

film. The in-plane birefringence was 0.12.

In a third embodiment, the uniaxial structure was induced when the optical

15   axis of the optical compensation film OO' was perpendicular to the plane of the

polymer film and $n_{OO'} > n_{\perp OO'}$ (positive C film, Figure 9 (d)). When fabricating this

film, the light beam was perpendicular to the plane of the polymer film. The actinic

light was non-polarized or circularly polarized. The film thickness was much less

than the characteristic absorption length, i.e., the light intensity was constant in the

20   film. The irradiation resulted in the anisotropy axis perpendicular to the polymer

surface. The value of light-induced birefringence depended on the exposure time

17

and light intensity. The sign of birefringence depended on the photosensitive fragment structure.

Example 3

5   Material: Structural formula of the material is given by

$$-\!\!\left(\!\!\begin{array}{c}CH-CH_2\end{array}\!\!\right)_{\!n}$$
$$|$$
$$COO$$
$$|$$
$$(CH_2)_6$$
$$|$$
$$O$$

[benzene ring]

$$N$$
$$\|\!|$$
$$N$$

[benzene ring]

$$OCH_4H_9$$
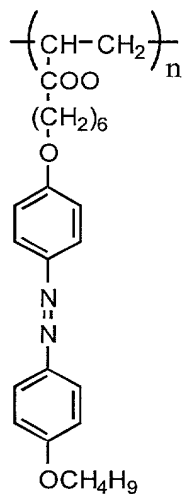
wherein n is a number from about 10 to about 1000. For this example, n was about 70.

Fabrication of the polymer film: The same as in Example 1.

10   Irradiation of the polymer film: The film was irradiated normally to the film plane with the parallel beam of the non-polarized light from a Xe-lamp. The intensity of the light was 11 mW/cm^2. The other conditions were the same as in Example 1. Characteristics of the film: The null ellipsometry technique showed uniaxial structure with orientation of the optic axis normally to the film; n_e-n_o=0.25.

15

Example 3a

Material: Structural formula of the material is given by

$$CH= CH_2$$
$$|$$
$$COO$$
$$|$$
$$(CH_2)_6$$
$$|$$
$$O$$

$$OC_4H_9$$
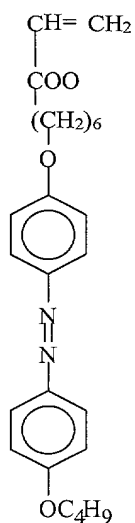
Photoinitiator Irgacure 369 from Ciba Additive, Inc. with a concentration of 10% by weight was added to the monomer in order to initiate polymerization of the material under irradiation with UV light. The prepared mixture was dissolved in dichloroethane at a concentration of 30 g/l.

Fabrication of the polymer film: The same as in Example 1.

Irradiation of the polymer film: The same as in Example 3.

Example 3b

Material: Structural formula of the material is given by
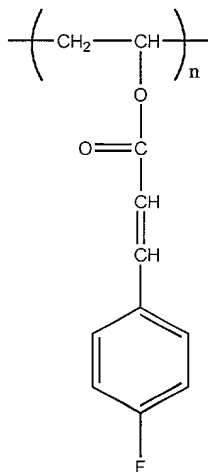
$$\left(\text{—CH}_2\text{—CH—}\right)_n$$
$$|$$
$$O$$
$$|$$
$$O\text{==}C$$
$$|$$
$$CH$$
$$\|$$
$$CH$$
$$|$$
$$\text{(benzene ring)}$$
$$|$$
$$F$$

wherein n is a number from about 10 to about 1000. For this example, n was about

5 200.

Fabrication of the polymer film: The same as in Example 1.

Irradiation of the polymer film: The same as in Example 3.

In a fourth embodiment, the uniaxial structure was induced when the optical

10 axis of the optical compensation film OO' was tilted to the plane of the polymer film and $n_{OO'} > n_{\perp OO'}$ (positive O plate Figure 9 (e)). The optical axis being tilted to the plane of the polymer film can be formed as follows. Polymer film is irradiated obliquely with actinic light. Polarization of the light is non-polarized or circularly polarized, and polymer material possesses the effect of reorientation of

15 photosensitive fragments perpendicular to the direction of light polarization, i.e. along the direction of light propagation in the film.

The optical axis being tilted to the plane of the polymer film can also be achieved as follows. Polymer film is irradiated obliquely with actinic light. The

20 light is non-polarized or circularly polarized and the polymer material possess the effect of light-induced anisotropy due to photo-transformation of the polymer fragments (decomposition, cross-linking, irreversible trans-cis isomerization, etc.). In this case, photosensitive fragments that are oriented parallel to the direction of

20

light propagation absorb light essentially weaker then that one oriented in other directions. The film thickness was much less than the characteristic absorption length, i.e., the light intensity was constant in the film.

5   In these case, generally, opical axis is induced in the direction parallel to the propagation direction of the light beam in the film, i.e. obliquely to the film plane. The sign of the light-induced birefringence depends on the photosensitive fragment structure and birefringence value is given by exposure and light intensity.

10   Example 4

Material: Structural formula of the material is given by

$$\left[\begin{array}{c} CH-CH_2 \\ | \\ COO \\ | \\ (CH_2)_6 \\ | \\ O \end{array} \right]_n$$
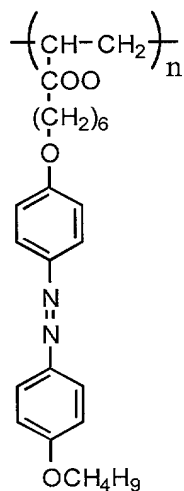
wherein n is a number from about 10 to about 1000. For this example, n was about 70.

15   Fabrication of the polymer film: The same as in the Example 1.

Irradiation of the polymer film: The film was irradiated in slope position with respect to the film plane with the parallel beam of the non-polarized light from a Xe-lamp. The angle between the light beam direction and the film plane was 45°. The other conditions are the same as in Example 1.

20

21

Characteristic of the film:

Film was investigated by null ellipsometry technique. It was described as uniaxial film with tilt position of the optic axis. The angle between film normal and direction of the optic axis is 19°; $n^e - n^o = 0.25$.
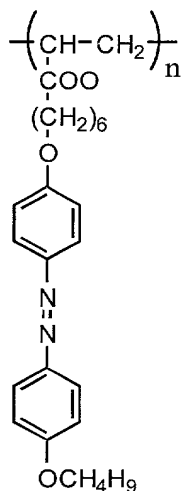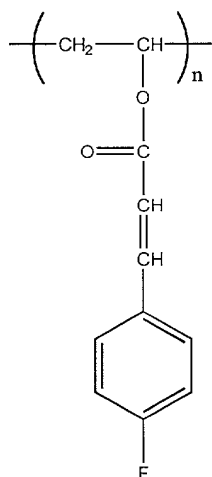
5

Example 4a

Material: Structural formula of the material is given by
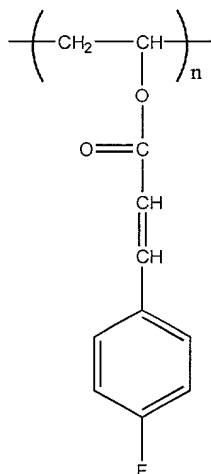
$$\left(\!-CH_2\!-\!\!\underset{\displaystyle \substack{| \\ O \\ | \\ O=C \\ | \\ CH \\ \| \\ CH}}{CH}\!-\!\right)_{\!n}$$

(benzene ring with F substituent)

wherein n is a number from about 10 to about 1000. For this example, n was about
10   200.

Fabrication of the polymer film: The same as in Example 2.

Irradiation of the polymer film: The same as in Example 4.

Characteristics of the film: After irradiation, the film was uniaxial with a tilt position of the optic axis. The angle between the film normal and direction of the
15   optic axis was 22° and $n_e - n_o = 0.01$.

In a fifth embodiment, a biaxial structure was induced when $n_x < n_y < n_z$ (Figure 9 c)). When fabricating this film, the light beam was directed perpendicularly or obliquely to the plane of the polymer film. The actinic light was
20   linearly, partially, or elliptically polarized. The film thickness was much less than the characteristic absorption length, i.e., the light intensity was constant in the film. The value of the light-induced birefringence depended on the exposure time and

22

light intensity. The sign of birefringence depended on the photosensitive fragment structure.

Example 5

5 Material: Structural formula of the material is given by

$$\left(\underset{\underset{\displaystyle \underset{\displaystyle O}{(CH_2)_6}}{COO}}{CH-CH_2} \right)_n$$

(benzene ring)

$$N$$
$$\parallel$$
$$N$$

(benzene ring)

$$OCH_4H_9$$

wherein n is a number from about 10 to about 1000. For this example, n was 70.

Fabrication of the polymer film: The same as in Example 1.

Irradiation of the polymer film: The same as in Example 1.

Characteristics of the film: After irradiation, the film was biaxial having in-plane

10 birefringence $n_y-n_x=0.05$ and out of plane $n_z-n_x=0.1$ (Figure 9 (e)).

Example 5a

Material: Structural formula of the material is given by

$$\left(\!-CH_2\!-\!\underset{\underset{\underset{\underset{\underset{\underset{\underset{F}{\bigcirc}}{|}}{CH}}{\overset{\|}{CH}}}{C}}{\overset{O=C}{\underset{|}{O}}}\!CH\!-\right)_{\!n}$$

wherein n is a number from about 10 to about 1000. For this example, n was about

5   200.

Fabrication of the polymer film: The same as in Example 2.

Irradiation of the polymer film: The same as in Example 1, except that irradiation

time was 60min.

Characteristics of the film: After irradiation, the film was biaxial having in-plane

10   birefringence n_y-n_x=0.005 and out of plane n_z-n_x=0.007 (Figure 9 (e)).

        The invention is not limited to the examples presented above.   More

complicated orientation structures could be induced by the use of several irradiation

steps.   Each step would differ by polarization and incident conditions of the light.

15

        The method of the present invention is useful for patterning of the

compensation film.   The structures described in Examples 1-5 could be realized in

each series of the domains.   The actinic light is non-polarized or polarized (linearly,

partially, or elliptically), directed normally or obliquely depending on the desired

20   structure in the domains.   Patterned structures could be realized by the use of a

mask system and multiple step irradiation.

Photo-modification of the structure of compensation film could be combined with the methods described earlier, for instance, mechanical treatment, alignment of LCs with aligning substrates, application of electrical or magnetic fields, and others.

5   Materials useful for the production of compensation films are not limited to the polymers and their corresponding monomers described in the examples above. Any material capable of acquiring anisotropic properties under irradiation may be capable for the fabrication of retardation films with the method described in the present invention.

10

The compensation layer could be coated on a separate substrate as well as on a substrate in a liquid crystal cell. The compensation film coated on the inner side of a substrate of a liquid crystal cell could simultaneously be used as an alignment layer for the liquid crystal cell.

15   It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.

CLAIMS

What is claimed is:

1. An optical compensation film for a liquid crystal display comprising a polymer capable of producing light induced anisotropy characterized in that the polymer has been irradiated with light to form at least one optical axis.

2. The optical compensation film of claim 1, wherein the polymer is selected from the group consisting of polyimides, methacrylates, acrylates, vinyls, vinyl ethers, siloxanes, styrene, epoxy polymers containing a functional group in at least one of a main chain and a side chain, and mixtures thereof, wherein the functional group is selected from the group consisting of azobenzene, stilbene, cinnamate, maleimide, coumarin, and mixtures thereof.

3. The optical compensation film of claim 1, wherein the polymer has been irradiated with light that is at least one of linearly polarized light, elliptically polarized light, circularly polarized light, partially polarized light, and non-polarized light.

4. The optical compensation film of claim 1, wherein the polymer has been irradiated a plurality of times.

5. The optical compensation film of claim 1, wherein the polymer has been irradiated a plurality of times and wherein the light on subsequent irradiations has at least one of a different polarization and a different angle with respect to a plane formed by the film.

6. The optical compensation film of claim 1, wherein the film is a plane and the optical axis is oriented to the plane in one of lying in the plane of the film, perpendicular to the plane of the film, tilted to the plane of the film, and changing across the film.

7. The optical compensation film of claim 1, wherein the film is a plane and has a biaxial structure, and the film has optical axes that are each one of oriented to the plane in one of lying in the plane of the film, perpendicular to the plane of the film, tilted to the plane of the film, and changing across the film, and wherein the optical axes are oriented different from each other.

8. A liquid crystal display comprising two opposed substrates, electrodes disposed on facing sides of the two opposed substrates, the optical compensation film of claim 1 disposed on at least one of the electrodes, and a liquid crystal disposed between the substrates.

9. A method of making a liquid crystal display cell containing an optical compensation film comprising: providing two opposed substrates, disposing the optical compensation film on at least one of the substrates on a surface of the substrate that faces the other substrate, irradiating the optical compensation film with light, disposing electrodes at one of i) on the substrate prior to disposing the optical compensation film, and ii) on the optical compensation film, disposing a liquid crystal between the substrates, and sealing the substrates together, wherein at least one optical axis is formed in the polymer film.

10. The method of claim 9, wherein the irradiation is at least one of linearly polarized light, elliptically polarized light, circularly polarized light, partially polarized light, and non-polarized light.

11. The method of claim 9, wherein the disposing is spin coating.

12. The method of claim 9, wherein the optical compensation film is a polymer selected from the group consisting of polyimides, methacrylates, acrylates, vinyls, vinyl ethers, siloxanes, styrene, epoxy polymers containing a functional group in at least one of a main chain and a side chain, and mixtures thereof, wherein the functional group is selected from the group consisting of azobenzene, stilbene, cinnamate, maleimide, coumarin, and mixtures thereof.

13. The method of claim 9, wherein the optical compensation film has been irradiated a plurality of times.

14. The method of claim 9, wherein the optical compensation film has been irradiated a plurality of times and wherein the light on subsequent irradiations has at least one of a different polarization and a different angle with respect to a plane formed by the film.

15. The method of claim 9, wherein the film is a plane and the optical axis is oriented to the plane in one of lying in the plane of the film, perpendicular to the plane of the film, tilted to the plane of the film, and changing across the film.

16. The method of claim 9, wherein the film is a plane and has a biaxial structure, and the film has optical axes that are each one of oriented to the plane in one of lying in the plane of the film, perpendicular to the plane of the film, tilted to the plane of the film, and changing across the film, and wherein the optical axes are oriented different from each other.

17. A method of making an optical compensation film comprising: providing a substrate; disposing a polymer in a solvent on the substrate; removing the solvent to form a polymer film; and irradiating the polymer with light, wherein at least one optical axis is formed in the polymer film.

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ABSTRACT OF THE INVENTION

An optical compensation film for a liquid crystal display is provided wherein the film is a polymer that is capable of producing light induced anisotropy. The film is irradiated with light to form an optical axis or axes.
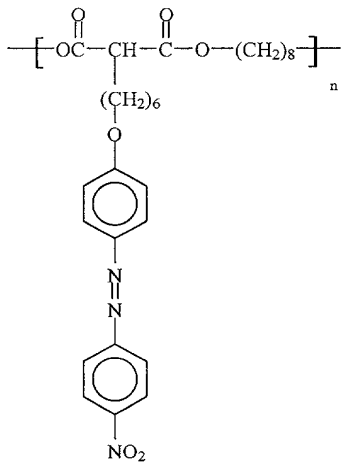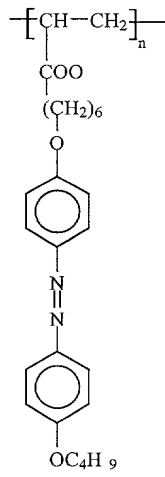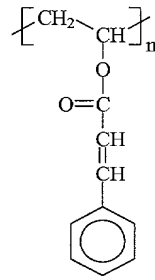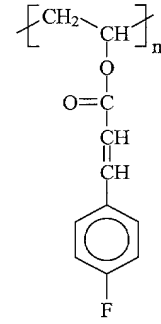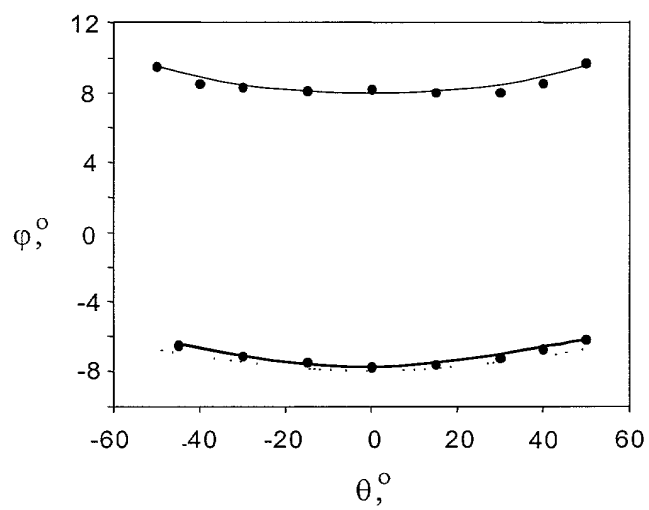
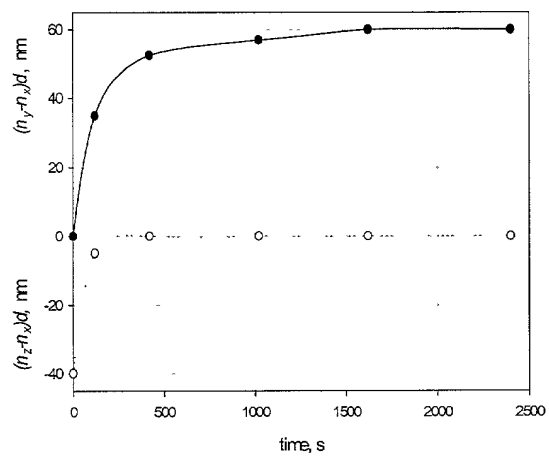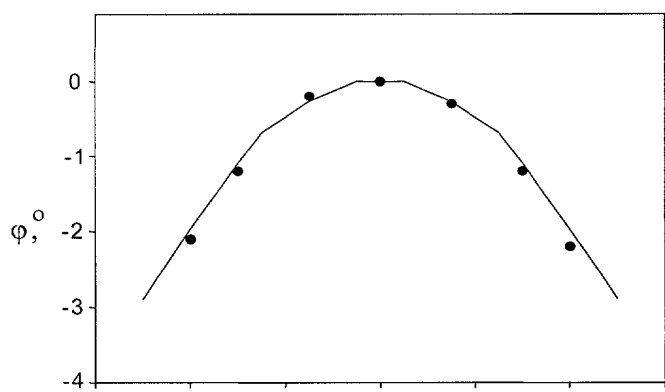FIG. 1A   FIG. 1B   FIG. 1C   FIG. 1D

FIG. 2
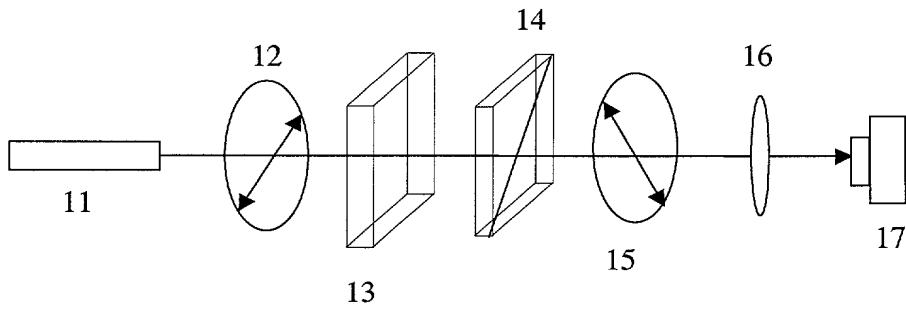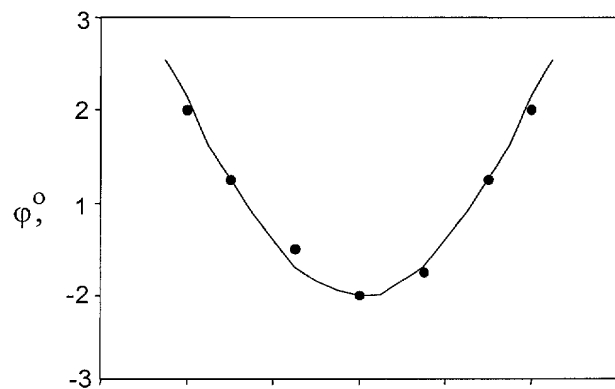
Fig. 3A

Fig. 3B

FIG. 4

FIG. 5A

FIG. 5B

FIG. 6

FIG. 7
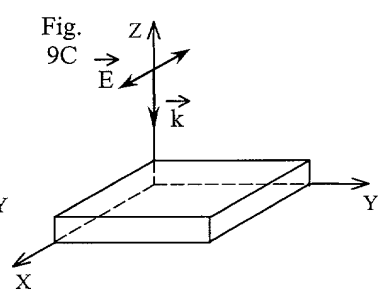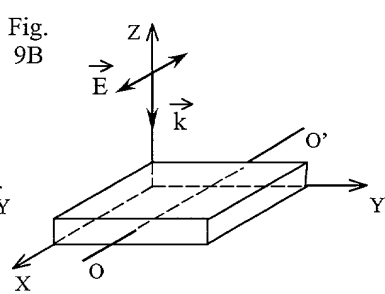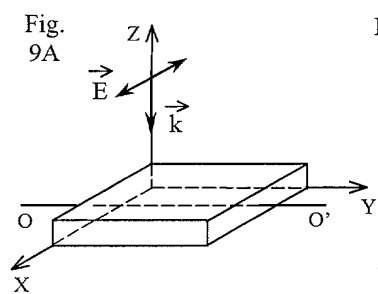
FIG. 8

Fig. 9A

Fig. 9B
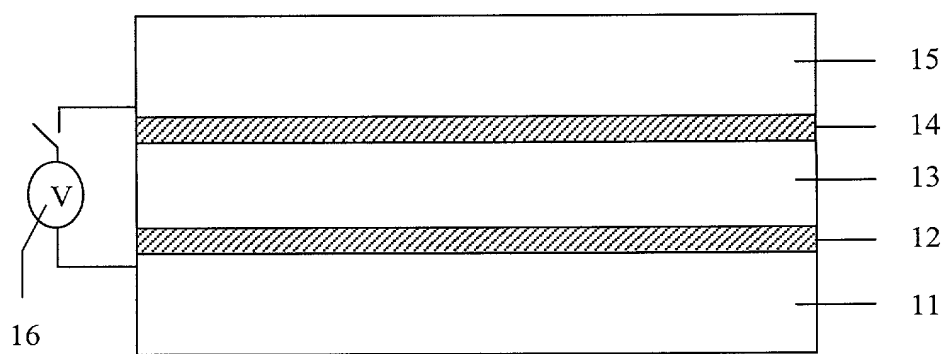
Fig. 9C

Fig. 9D

Fig. 9E
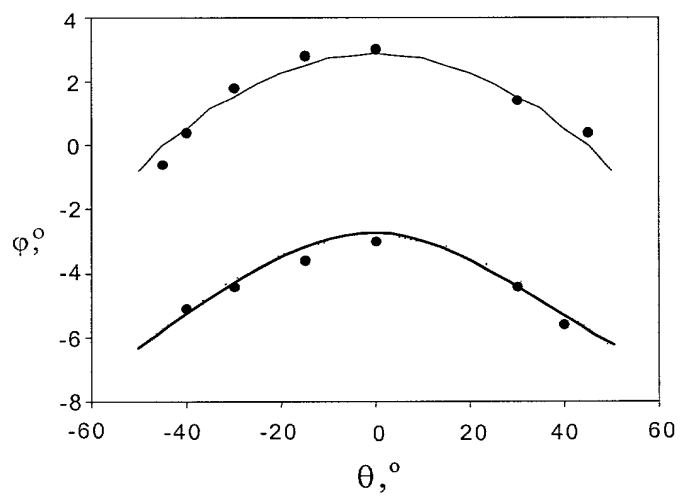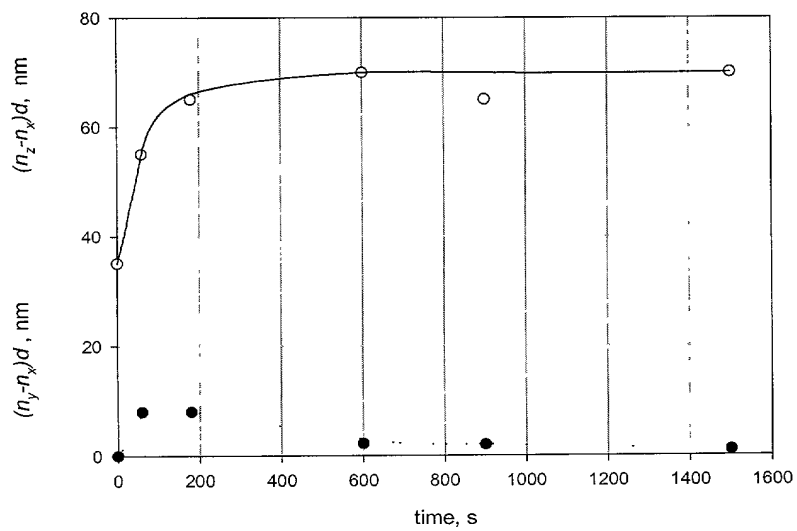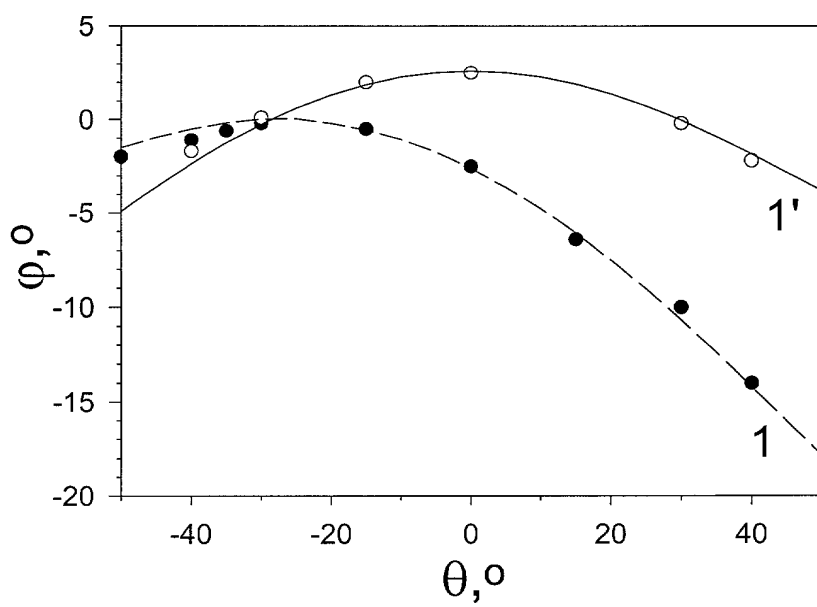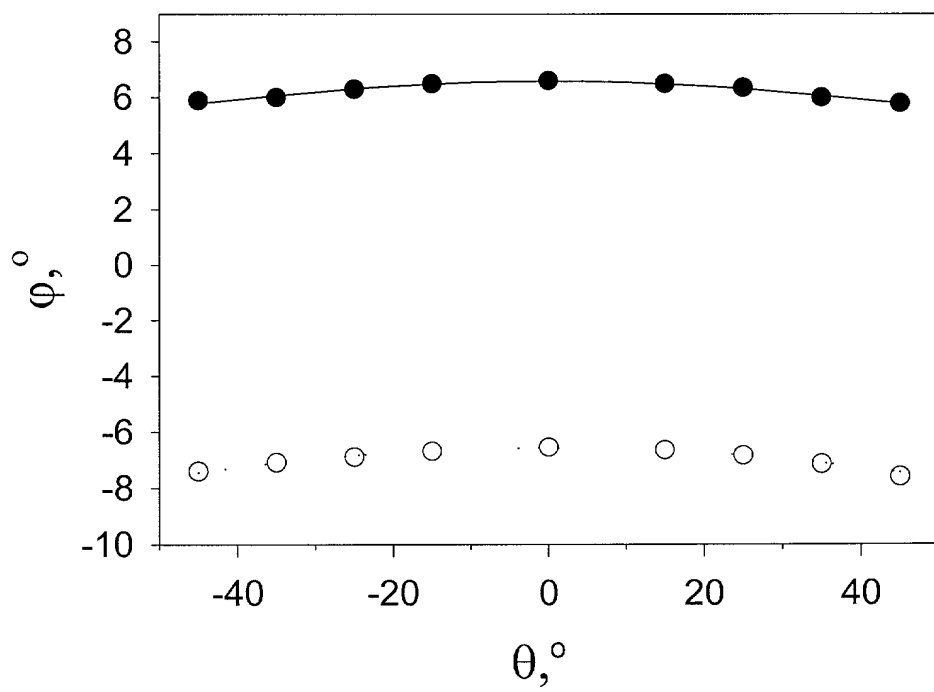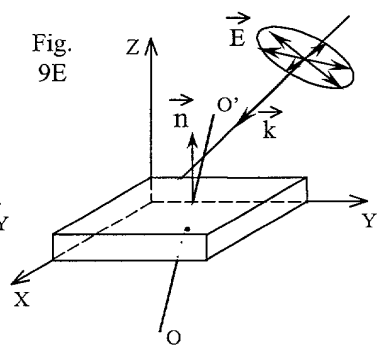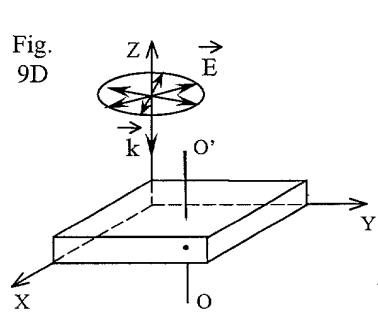
FIG. 10

DECLARATION AND POWER OF ATTORNEY

As below named inventors, we hereby declare that:

Our residence, post office address and citizenship are as stated below next to our names.

We believe we are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Optical Compensation Film for Liquid Crystal Display

including any amendments referred to below, the specification of which

    __X__ is attached hereto.

    _____ was filed on _____ as Application Serial No. _____ and

    _____ was amended on _____.

We hereby state that we have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

We hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Provisional Application Number	Filing Date

We hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, we acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status

We hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Priority Claimed

Number	Country	Date Filed	Yes	No
Number	Country	Date Filed	Yes	No

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY:

As named inventors, we hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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